

CHARACTERIZATION AND STABILITY PROPERTIES OF POLAR EXTRACTS DERIVED FROM A RECENT SHALE LIQUID

John V. Cooney*, George W. Mushrush and Erna J. Beal

Naval Research Laboratory, Code 6180, Washington, D.C. 20375-5000

INTRODUCTION

Recent studies into the mechanisms of storage instability with middle distillate fuels have indicated that the presence of polar compounds, particularly nitrogen heterocycles, is frequently related to the deterioration of aged fuel samples [1-5]. In certain instances, direct autoxidation of nitrogen containing species is indicated, which may be subject to catalytic effects made possible by trace fuel components [6,7]. At other times, the organic nitrogen compounds themselves assume the role of catalyst in the oxidation of other fuel molecules. One approach to the problem of nitrogen compound induced storage instability has involved model compound dopant studies [8,9]. A second approach involves the study of the stability properties of actual high-nitrogen middle distillate fuels [10,11]. In this paper we discuss the second approach which was applied to a recently refined high-nitrogen shale liquid. Thus, polar extract components were isolated, characterized and studied in the context of accelerated storage stability tests.

EXPERIMENTAL

The high-nitrogen shale liquid which was examined in this study was refined from Geokinetics crude shale oil refined at the Caribou-Four Corners Refinery (Utah). The sample which was studied had been distilled and partially hydrotreated, and was designated at NRL as "fuel 83-65". Fuel 83-65 is identical to processing intermediate 1-HTR-3 recently studied by Thompson and Holmes [12]. Fuel 83-65 was separated into three polar extracts using a reported procedure involving extraction with acid (1.0 N HCl) followed by batch adsorption onto silica gel, which was subsequently back-washed with methylene chloride and methanol [10,11]. The three extracts thus provided were: (a) BNC ("basic nitrogen compound" extract, the acid-extractable material, in methylene chloride), (b) NBNC(CH₂Cl₂) ("non-basic" extract in methylene chloride), and (c) NBNC(CH₃OH) (methanolic wash of the silica gel). The polar extracts were examined by capillary GC/MS using reported conditions [10].

The accelerated storage stability test method used has been described in detail [4]. In summary, 300 ml samples of filtered fuel were thermally stressed in the dark in 500 ml screw-cap borosilicate Erlenmeyer flasks (Teflon-lined caps). Replicate samples were run, with both filterable sediment and adherent gum values determined after storage. Peroxide numbers (ASTM D1583-60) were also determined in samples of filtered fuel before and after stress. Extract-doping experiments employed a very stable Navy Shale-II process shale diesel fuel, fuel D-11, as diluent. Fuel

D-11 has been well-characterized and contains AO-30 (2,4-dimethyl-6-t-butylphenol) as the sole additive [4]. All extracts were stripped of their solvent (verified by GC) by gentle rotary evaporation prior to being added to fuel D-11. Nitrogen concentration levels in fuel samples were determined by a chemiluminescent technique with an Antek Model 720 instrument [4,10].

RESULTS AND DISCUSSION

Preliminary accelerated storage stability tests at 43°C and 80°C indicated that shale fuel 83-65 possessed marginal stability (Table I). The fuel was found to be relatively high in nitrogen content, containing 2290 ppm N (w/v). It was consequently of interest to us to examine the polar components of this shale liquid as part of an effort to relate fuel composition to stability behavior [10]. The high nitrogen content of fuel 83-65 permitted the convenient extraction of a significant amount of polar material for use in the subsequent doping experiments. In addition to these preliminary tests, the shale liquid was subjected to a simulated distillation analysis. Fuel 83-65 was found to be a broad-cut fraction. By ASTM D2887, IBP was 120°C, 50% was 299°C, 95% was 421°C and FBP was 485°C. Correlation to ASTM D86 gave IBP of 190°C, a 50% value of 306°C and a 95% value of 423°C. No hydroperoxide was detected in fuel 83-65 prior to or following storage stability testing (i.e., peroxide numbers were 0.0 by ASTM D1583-60).

Table I

Accelerated Storage Stability Results for Fuel 83-65 (unvented - mg/100 ml)

| <u>Storage Conditions</u> | <u>Filtered Sediment</u> | <u>Adherent Gum</u> | <u>Total Insolubles</u> | | |
|---------------------------|--------------------------|---------------------|-------------------------|-------------|-----------------|
| | | | <u>Duplicate</u> | <u>Mean</u> | <u>Std.Dev.</u> |
| 80°C-7 days | 2.3 | 0.6 | 2.9 | 2.8 | ±0.1 |
| | 1.7 | 1.1 | 2.8 | | |
| | 1.8 | 1.0 | 2.8 | | |
| 80°C-14 days | 4.5 | 2.6 | 7.1 | 7.4 | ±1.1 |
| | 3.7 | 4.9 | 8.6 | | |
| | 3.5 | 2.9 | 6.4 | | |
| 43°C-49 days | 1.6 | 0.6 | 2.2 | 2.5 | ±0.4 |
| | 1.8 | 1.1 | 2.9 | | |
| | 0.8 | 1.6 | 2.4 | | |
| 43°C-91 days | 2.5 | 2.2 | 4.7 | 4.9 | ±0.4 |
| | 2.4 | 2.2 | 4.6 | | |
| | 2.1 | 3.2 | 5.3 | | |

Extraction of Nitrogen Compounds

The separation scheme which was used for the removal of polar extracts was patterned after an earlier procedure [10]. A single, mild acid extraction (using 3.67 equiv. of 1.0 N HCl) was selected to minimize the opportunity for chemical changes in the fuel. The BNC extract was obtained in methylene chloride following neutralization of the acid wash. Subsequent treatment of the acid extracted fuel with active silica gel afforded two NBNC extracts (in methylene chloride and methanol). The fuel and extracts were analyzed for soluble nitrogen content in order to assess a nitrogen balance (Table II). It was possible (within analytical error) to account for nearly all of the nitrogen originally present in fuel 83-65. The accelerated storage stability of fuel 83-65 was improved by the acid/silica treatment, with only ca. 2.4 mg/100 ml of total insolubles resulting after 14 day - 80° stress (cf. 7.4 mg/100 ml before extraction).

Table II

Nitrogen Analyses for Extracted Fuel 83-65

| <u>Sample</u> | <u>N Concentration (ppm w/v)</u> |
|---|----------------------------------|
| 1. Original | 2290 |
| 2. After acid extraction | 700 |
| 3. Isolated in CH ₂ Cl ₂ wash of silica | 490 |
| 4. Isolated in CH ₃ OH wash of silica | 75 |
| 5. After acid and silica treatment | 130 |

Examination of Polar Fuel Extracts

Components of the BNC, NBNC(CH₂Cl₂) and NBNC(CH₃OH) extracts were examined by GC/MS by a procedure which has been reported [10]. The results for the acid extractable material (BNC) and the NBNC(CH₃OH) extract are given together in Table III. Table III indicates that both of these extracts were rich in nitrogen heterocycles, principally alkylpyridines. The pyridines which were in the BNC extract were characterized by long alkyl chains (unbranched) while the NBNC(CH₃OH) extract pyridines were highly branched and generally of a higher molecular weight. Table IV compares the identifications of the ten largest peaks found in these two extracts. The presence of a substantial amount of tetrahydroquinolines (ca. 29%) in the BNC extract is a reflection of the hydrotreatment used during processing. For all three polar fuel extracts, over 95% of the total sample peak area was identified, so that the peaks which were examined were representative of the samples.

Table III
Examination of BNC and NBNC(CH₃OH) Extracts from Fuel 83-65

| Compound Class* | BNC Extract | | NBNC(CH ₃ OH) Extract | |
|-------------------------|-------------|--------|----------------------------------|--------|
| | n | Area % | n | Area % |
| A. Pyridines | (175) | (60.2) | (213) | (88.6) |
| <C ₄ | 12 | 0.7 | 6 | 0.6 |
| C ₄ | 5 | 0.6 | 7 | 1.5 |
| C ₅ | 19 | 0.6 | 15 | 0.6 |
| C ₆ | 10 | 0.2 | 1 | <0.1 |
| C ₇ | 14 | 9.8 | 3 | 0.1 |
| C ₈ | 20 | 16.4 | 6 | 0.1 |
| C ₉ | 24 | 14.6 | 6 | 0.1 |
| C ₁₀ | 22 | 9.9 | 10 | 0.8 |
| C ₁₁ | 43 | 6.3 | 15 | 1.9 |
| C ₁₂ | 6 | 1.2 | 28 | 5.5 |
| C ₁₃ | - | - | 34 | 27.9 |
| C ₁₄ | - | - | 39 | 26.4 |
| C ₁₅ | - | - | 34 | 12.7 |
| C ₁₆ | - | - | 9 | 10.3 |
| B. Tetrahydroquinolines | (134) | (29.0) | (114) | (5.7) |
| <C ₃ | 6 | 0.6 | 2 | 0.2 |
| C ₃ | 13 | 2.9 | 9 | 0.5 |
| C ₄ | 19 | 12.8 | 2 | 0.1 |
| C ₅ | 23 | 6.6 | 3 | 0.1 |
| C ₆ | 29 | 3.2 | 5 | 0.1 |
| C ₇ | 35 | 2.2 | 32 | 1.7 |
| C ₈ | 8 | 0.6 | 17 | 1.0 |
| C ₉ | 1 | 0.2 | 25 | 0.8 |
| C ₁₀ | - | - | 12 | 0.5 |
| C ₁₁ | - | - | 7 | 0.7 |
| C. Quinolines | (54) | (7.9) | (12) | (0.2) |
| <C ₃ | 2 | 0.4 | - | - |
| C ₃ | 7 | 2.1 | - | - |
| C ₄ | 12 | 1.6 | - | - |
| C ₅ | 18 | 3.2 | - | - |
| C ₆ | 13 | 0.7 | - | - |
| C ₇ | 2 | <0.1 | - | - |
| D. Indoles | (40) | (2.2) | (20) | (1.3) |
| <C ₇ | 10 | 0.7 | - | - |
| C ₇ | 9 | 0.5 | - | - |
| C ₈ | 18 | 0.8 | - | - |
| C ₉ | 3 | 0.1 | - | - |
| E. Carbazoles | (-) | (-) | (98) | (3.2) |
| <C ₄ | - | - | 8 | 0.1 |
| C ₄ | - | - | 22 | 0.5 |
| C ₅ | - | - | 38 | 1.1 |
| C ₆ | - | - | 22 | 1.3 |
| C ₇ | - | - | 5 | 0.1 |
| C ₈ | - | - | 3 | 0.1 |
| F. Other N Compounds | (16) | (0.8) | (16) | (0.4) |
| G. Other Compounds | (-) | (-) | (19) | (0.6) |

*"C_x" denotes the no. of carbon atoms in substituents on the heterocyclic ring, "n" is the number of isomers observed, "Area %" is based on the total ion count from mass of 45 through 450.

Table IV

A. Ten Largest Peaks - BNC Extract From Fuel 83-65

| <u>Rank</u> | <u>Rel. Area</u> | <u>Main Component</u> | <u>Retention Time (min)</u> |
|-------------|------------------|--------------------------------------|-----------------------------|
| 1 | 1000 | Dimethylhexylpyridine | 27:16 |
| 2 | 913 | Methylpropyltetrahydroquinoline | 26:26 |
| 3 | 870 | Trimethylpentylpyridine | 26:15 |
| 4 | 854 | Dimethylheptylpyridine | 30:32 |
| 5 | 825 | Dimethylhexylpyridine | 28:10 |
| 6 | 775 | Dimethylpentylpyridine | 23:51 |
| 7 | 676 | Trimethylhexylpyridine | 29:30 |
| 8 | 660 | a C ₄ Tetrahydroquinoline | 25:59 |
| 9 | 472 | Trimethylhexylpyridine | 28:58 |
| 10 | 413 | a C ₈ Pyridine | 27:07 |

B. Ten Largest Peaks - NBNC(CH₃OH) Extract From Fuel 83-65

| <u>Rank</u> | <u>Rel. Area</u> | <u>Main Component</u> | <u>Retention Time (min)</u> |
|-------------|------------------|----------------------------|-----------------------------|
| 1 | 1000 | a C ₁₃ Pyridine | 37:48 |
| 2 | 549 | Trimethyltridecylpyridine | 47:12 |
| 3 | 544 | a C ₁₃ Pyridine | 38:09 |
| 4 | 495 | a C ₁₆ Pyridine | 47:15 |
| 5 | 375 | Trimethylundecylpyridine | 42:26 |
| 6 | 317 | Trimethyldecylpyridine | 39:53 |
| 7 | 281 | Dimethyltridecylpyridine | 45:19 |
| 8 | 260 | Trimethylundecylpyridine | 40:49 |
| 9 | 251 | Dimethylundecylpyridine | 40:14 |
| 10 | 238 | Trimethylundecylpyridine | 43:29 |

The methylene chloride NBNC extract was found to be very complex, consisting primarily of hydrocarbons. Most of the nitrogen in this extract appeared in the form of substituted indoles. The compound classes present are summarized in Table V.

Table V

Examination of NBNC(CH₂Cl₂) Extract From Fuel 83-65

| <u>Compound Class</u> | <u>No. Isomers</u> | <u>Area %</u> |
|------------------------------|--------------------|---------------|
| A. <u>Hydrocarbons</u> | (294) | (91.3) |
| Alkanes | 33 | 44.8 |
| Cycloalkanes | 35 | 2.1 |
| Benzenes | 80 | 10.7 |
| Naphthalenes | 22 | 8.5 |
| Tetralins | 53 | 11.1 |
| Indanes | 15 | 2.8 |
| Fluorenes | 15 | 4.2 |
| Phenanthrenes | 9 | 3.8 |
| Biphenyls | 11 | 2.1 |
| Other Hydrocarbons | 21 | 1.2 |
| B. <u>Nitrogen Compounds</u> | (37) | (8.7) |
| Indoles | 27 | 6.0 |
| Other Nitrogen Compounds | 10 | 2.8 |

Results of Doping Experiments

The polar components of each of the three extracts were added as dopants to a stable shale diesel fuel (fuel D-11). Stress conditions employed temperatures of 80°C and 43°C for periods of time ranging up to 14 and 154 days respectively [8,10]. The results of the doping experiments are given in Table VI. In the table, the amount of total insoluble material is reported as the mean of three experimental trials.

Table VI

Total Insolubles for D-11 with Added Polar Extracts

| <u>Extract</u> | <u>Storage Conditions</u> | <u>N Added (ppm-w/v)</u> | <u>Total Insolubles(mg/100 ml)</u> | |
|--|---------------------------|--------------------------|------------------------------------|------------------|
| | | | <u>Mean</u> | <u>Std. Dev.</u> |
| BNC | 80°C-7d | 337 | 1.6 | ±0.2 |
| | 80°C-14d | 337 | 1.3 | ±0.6 |
| | 43°C-77d | 337 | 0.5 | ±0.0 |
| | 43°C-154d | 337 | 0.7 | ±0.1 |
| NBNC(CH ₂ Cl ₂) | 80°C-7d | 264 | 4.3 | ±0.6 |
| | 80°C-14d | 264 | 4.7 | ±0.6 |
| | 43°C-70d | 264 | 4.1 | ±0.2 |
| NBNC(CH ₃ OH) | 80°C-14d | 163 | 63.7 | ±22.5 |
| undoped D-11 | 80°C-14d | 0 | 0.0 | ±0.1 |
| | 43°C-52d | 0 | 0.1 | ±0.2 |
| | 43°C-154d | 0 | 0.4 | ±0.0 |

The results of the dopant experiments indicated that the methanolic NBNC extract was by far the most active sediment promoter in the D-11 fuel, about as active as 2,5-dimethylpyrrole on a ppm N (w/v) basis [4]. This is the most active fuel extract we have yet isolated; it is considerably more reactive than the NBNC(CH₃OH) extracts obtained from other shale fuels in earlier work [10]. Notable constituents of the methanolic NBNC extract were branched alkylpyridines as well as alkylcarbazoles, which have yet to be studied as model dopants in well-defined systems [4]. We speculate that these species may be involved in the oxidation reactions of storage instability. It was surprising to isolate such a reactive extract from fuel 83-65, since the fuel is actually quite a bit more stable than other shale fuels which we have studied (cf. Table I and ref. 10). This clearly indicates the importance of complex "interactive effects" present in a given fuel in controlling and allowing the expression of oxidative lability of sensitive molecules [7]. Thus, it is possible that natural antioxidants present in fuel 83-65 normally suppress the tendency of the components of extract NBNC(CH₃OH) to oxidize or initiate oxidation processes.

The NBNC(CH₂Cl₂) extract was found to be a mild promoter of instability, while the BNC extract had little effect despite the fact that some 337 ppm N (w/v) had been added to the D-11 base fuel. The inertness of the BNC extract may be a result of reduced oxidizability of straight-chain alkylpyridines (relative to branched) or may be due to inhibition as a result of the high tetrahydroquinoline content [10]. Instability promoted by the NBNC(CH₂Cl₂) extract may be a consequence of the presence of modest amounts of olefins and alkylindoles in this extract.

CONCLUSIONS

Polar fractions have been isolated and characterized from a recently refined shale-derived liquid. When the extracts were added as dopants to a stable shale diesel fuel and stored at elevated temperatures, the formation of insoluble material was observed. The most active extract in promoting instability consisted primarily of branched alkylpyridines (not acid-extractable) together with modest amounts of tetrahydroquinolines and alkylcarbazoles.

ACKNOWLEDGEMENT

This work was funded by the Department of Energy under an interagency agreement, contract no. DE-AI-19-81-BC10525. References to brand names were made for identification only and do not imply endorsement by DOE or NRL.

LITERATURE CITED

- (1) Frankenfeld, J.W., Taylor, W.F. and Brinkman, D.W., U.S. Department of Energy Report No. DOE/BC/10045-12 (1981).
- (2) Frankenfeld, J.W., Taylor, W.F. and Brinkman, D.W., Ind. Eng. Chem. Prod. Res. Dev., 22, 608, 615, 622 (1983).
- (3) Goetzinger, J.W., Thompson, C.J. and Brinkman, D.W., U.S. Department of Energy Report No. DOE/BETC/IC-83/3 (1983).
- (4) Cooney, J.V., Beal, E.J. and Hazlett, R.N., Liq. Fuels Tech., 2, 395 (1984).
- (5) Dahlin, K.E., Daniel, S.R. and Worstell, J.H., Fuel, 60, 477 (1981); Worstell, J.H. and Daniel, S.R., Fuel, 60, 481 (1981); Worstell, J.H., Daniel, S.R. and Fraunhöff, G., Fuel, 60, 485 (1981).
- (6) Frankenfeld, J.W., Taylor, W.F. and Brinkman, D.W., U.S. Department of Energy Report No. DOE/BC/10045-23 (1982).
- (7) Cooney, J.V., Beal, E.J. and Beaver, B.D., Preprints, Div. of Fuel Chem., ACS, 30, in press (1985).
- (8) Cooney, J.V., Beal, E.J. and Hazlett, R.N., Preprints, Div. of Petro. Chem., ACS, 28, 1139 (1983).
- (9) Cooney, J.V., Beal, E.J., Wechter, M.A., Mushrush, G.W. and Hazlett, R.N., Preprints, Div. of Petro. Chem., ACS, 29, 1003 (1984).
- (10) Cooney, J.V., Beal, E.J. and Hazlett, R.N., Preprints, Div. of Petro. Chem., ACS, 29, 247 (1984).
- (11) Cooney, J.V., Beal, E.J. and Hazlett, R.N., Ind. Eng. Chem. Prod. Res. Dev., in press (1985).
- (12) Thompson, L.F. and Holmes, S.A., Fuel, 64, 9 (1985).